



Two-step sequence for synthesis of efficient PtSn@Rh/C catalyst for oxidizing ethanol and intermediate products

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ABSTRACT

PtSn@Rh/C-HT catalysts were designed and synthesized by a two-step sequence synthesis: Rh was firstly deposited on the carbon support and then PtSn through microwave assisted polyol method, followed by the heat treatment (HT) in a reductive atmosphere. This well-designed process provided PtSn@Rh/C-HT with a desirable electrocatalytic activity towards the electrooxidation of ethanol as well as its intermediate products. Especially, for the acetic acid electrooxidation, PtSn@Rh/C-HT behaved quite different from Pt/C, PtSn/C, PtSn@Rh/C without heat-treatment, and PtSnRh/C fabricated through one-step method, without the characteristic peaks for hydrogen adsorption–desorption but significant oxidation current of acetic acid. This gives a platform for taking full advantage of the joint synergistic effect among Pt, Sn and Rh for direct ethanol fuel cell applications.

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1. Introduction

Rhodium (Rh) has brought the promise for ethanol electrooxidation with high activity and high selectivity towards CO₂ over Pt-based catalysts [1–5]. Recently, Adzic's group [6] developed a ternary PtRhSnO₂/C, which can break the C–C bond of ethanol molecule at room temperature in acid solution and facilitate its oxidation to CO₂ at low potentials through oxametallacyclic conformation. Based on their experimental and theoretical results, the above desirable electrocatalytic activity depends on the joint synergistic effect between these three constituents. That is, Pt provides the active sites for the first step of adsorption and dehydrogenation of ethanol, while Rh plays the main role in the preference for the CH₂CH₂O conformation, and thus leading to the direct C–C bond cleavage, which agrees well with the effect of Rh addition at the metal–gas interface, showing the preference for the CH₂CH₂O conformation [7]. Simultaneously, SnO₂ can strongly adsorb H₂O under electrochemical conditions, which is of importance to provide OH[−] for the further oxidation of adsorbed CO over Rh or Pt, and at the same time to make Pt and Rh free to oxidize ethanol. Then, Kowal et al. further optimized the PtRhSnO₂ ternary catalysts from the point of view of components and their atomic ratio. They found

that Pt–Rh–SnO₂/C electrocatalyst with an optimum atomic ratio of Pt:Rh:Sn = 3:1:4 exhibited highest oxidation currents, lower onset potential, and capability to split the C–C bond of ethanol molecule at room temperature [8,9]. Very recently, it has been found that Pt₅₂Sn_(36−x)Rh₁₂–Sn_xO_{2x} catalysts, with the coexistence of homogeneously distributed Pt/Sn/Rh random alloy and non-alloyed SnO₂ throughout the catalyst, possessed a superior long-term activity and stability towards ethanol oxidation than the commercial Pt catalyst [10].

On one hand, as discussed above it has been known that the combined effect of Pt, Rh and Sn does give a desirable activity for ethanol electrooxidation. On the other hand, how to make full use of this ternary PtRhSn catalyst to exhibit the further improved activity and high selectivity towards CO₂ needs further investigation. Catalyst's preparation method is the key of achieving the desired activity, selectivity and life time [11]. Obviously, the synthesis strategies play a determining role in the catalyst's properties including morphology, textures and forms, activity, stability, and so on.

In the present investigation, we report a two-step sequence synthesis of PtSnO₂@Rh/C-HT catalysts by a modified pulse microwave assisted polyol method, followed by heat treatment for achieving the enhanced mutual effect between the active components. It has been found that the as-obtained PtSnO₂@Rh/C-HT exhibited a relatively high activity not only towards ethanol electrooxidation but also towards the further oxidation of its intermediate products, i.e. acetaldehyde and acetic acid. Especially, in the case of acetic acid oxidation, there is an obvious oxidation current

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observed, indicating the C–C bond cleavage at PtSnO₂@Rh/C-HT electrode.

2. Experimental part

2.1. Catalyst preparation

XC-72 carbon black (Cabot Corp.) supported Pt–Sn–Rh ternary catalysts (with a Pt/Sn/Rh atomic ratio of 3:4:1, 20 wt% noble metal) catalysts were synthesized through a two-step sequence by a modified pulse-microwave assisted polyol method [12,13]. Firstly, Rh/C was obtained by the following procedure. An appropriate amount of RhCl₃ was well mixed with ethylene glycol (EG) in an ultrasonic bath, and then the carbon black was added into the mixture. After the pH value of the system was adjusted to more than 10 by the drop-wise addition of 2.0 mol L⁻¹ NaOH/EG, a well-dispersed slurry was obtained with stirring and ultrasonication for 30 min. Thereafter, the slurry was microwave-heated in a 10 s-on/10 s-off pulse form for several times and then re-acidified. Finally, the resulting black solid sample was filtered, washed until no chloride anion in the filtrate could be detected by 1.0 mol L⁻¹ AgNO₃ aqueous solution and then dried at 80 °C for 12 h in a vacuum oven. The above process was repeated except that H₂PtCl₆·6H₂O and SnCl₂ as the respective Pt and Sn precursors were introduced and the as-prepared Rh/C replaced carbon black as the support. The obtained catalysts are denoted as PtSn@Rh/C-AP (as prepared). Furthermore, in order to strengthen the interaction among these three components, the as-prepared PtSn@Rh/C was heat treated in H₂ (5%) + Ar (95%) atmosphere at 300 °C for 1 h and this sample was denoted as PtSn@Rh/C-HT (heat-treated). For the sake of comparison, PtSnRh/C-HT was also prepared through one-step method following the same heat treatment.

2.2. Catalyst characterization

The X-ray Diffraction (XRD) measurements were carried out by the aid of a D/Max-III A (Rigaku Co., Japan) employing Cu K_α (λ = 0.15406 nm) as the radiation source was set at 40 kV and 40 mA. The morphology of the as-prepared catalysts was obtained by Transmission Electron Microscopy (TEM). For sample preparation, the catalysts were ultrasonically dispersed in ethanol solution to get uniform catalyst ink and fixed onto a copper grids covered with holey carbon film. The TEM investigations were performed on a JEOL TEM-2010 (HR) operating at 200 kV.

All the electrochemical measurements were conducted on a CHI660 instrument in a three-electrode cell mounted in a thermostatic water bath, with a saturated calomel electrode (SCE) as the reference electrode and a platinum foil as the counter electrode, respectively. The thin catalyst film was prepared onto the glassy carbon disk surface with a diameter of 0.5 cm. Typically, a mixture containing 5.0 mg electrocatalyst, 1.8 mL ethanol and 0.2 mL Nafion solution (5 wt%, DuPont, USA) was ultrasonicated for 15 min to obtain a well-dispersed ink. The catalyst ink was then quantitatively transferred onto the surface of the glass carbon electrode and dried under infrared lamp to obtain a catalyst thin film. The electrochemical tests were performed in 0.5 mol L⁻¹ H₂SO₄ aqueous solutions containing: (a) 1.0 mol L⁻¹ C₂H₅OH, (b) 0.5 mol L⁻¹ CH₃CHO, and (c) 0.5 mol L⁻¹ CH₃COOH respectively, for the electrochemical activity evaluation. The current densities were obtained by dividing the obtained current in mA by the geometric area of glassy carbon disk in square centimeter. Before each experiment, the electrolyte solution was bubbled with high-purity N₂ for 30 min in order to remove the dissolved oxygen inside. It should be noted that without specification, all

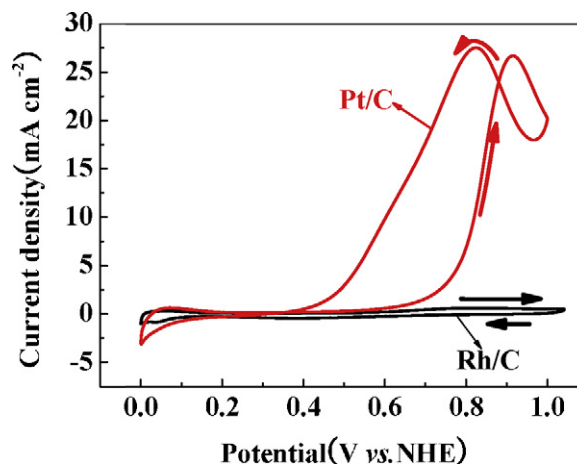


Fig. 1. CV curves for ethanol electrooxidation over Pt/C and Rh/C in 0.5 mol L⁻¹ H₂SO₄ + 1.0 mol L⁻¹ C₂H₅OH. Scan rate: 50 mV s⁻¹, 30 °C.

the potentials are referred to the normal hydrogen electrode (NHE).

3. Results and discussion

It can be clearly seen from Fig. 1 that, unlike Pt/C, Rh/C exhibits almost no activity towards ethanol electrooxidation. Moreover, it has been recognized that it is Pt that acts as the active site for ethanol adsorption and dissociation, while Rh just play a contributing and synergistic role for ethanol electrooxidation [6]. Accordingly, in the case of PtSnRh/C ternary catalysts, if part of Pt particles were covered by Rh atoms, the starting steps for ethanol electrooxidation could be blocked and then the activity would be decreased. On the other hand, up to now PtSnRh/C ternary catalysts are mainly prepared by the co-deposition method, where Pt, Sn and Rh precursors are firstly mixed together and then the reducing agents are introduced. Based on the reported results, PtSn catalysts obtained through the co-deposition of Pt and Sn can possess high activity towards ethanol electrooxidation [14–16].

However, what will be the situation when Rh is introduced? To answer this question, we monitored the reduction procedure of PtCl₆²⁻ and Rh³⁺ in EG by adopting NaBH₄ as the reducing agent. The corresponding photos at different time with visible change are taken and given in Fig. 2. Obviously, in the case of PtCl₆²⁻ EG solution, the yellow color changes into brown in 13 s and into inkiness in 15 s. While in the other case of Rh³⁺ EG solution, the solution color starts to change from yellow to light brown until 34 s after the addition of NaBH₄ with the same amount as the case of PtCl₆²⁻ EG solution. Up to 74 s, the solution color becomes brown like PtCl₆²⁻ EG solution at 13 s. In about 120 s, an inkiness mixture was just obtained. According to the information of the inorganic chemistry, when the metal ions have not been completely reduced, the solution shows the color of metal ions. After the metal ions have been reduced into metal atoms, these atoms aggregate into small particles. Then the black color is observed. As a result, it is easily inferred that the reduction of Rh³⁺ to Rh⁰ is more difficult than that of PtCl₆²⁻ to Pt⁰. Accordingly, if the codepositon method is adopted for Pt and Rh reduction, part of Pt active sites could be blocked by Rh atoms, leading firstly to small electrochemical surface area of Pt and consequently to low electrocatalytic activity towards ethanol electrooxidation.

So, we wish this can be avoided by adopting a two-step sequence to synthesize PtSn@Rh/C catalysts by the pulse microwave assisted polyol method as schematically given in Fig. 3. The detailed preparation procedure was described above in the experimental part.

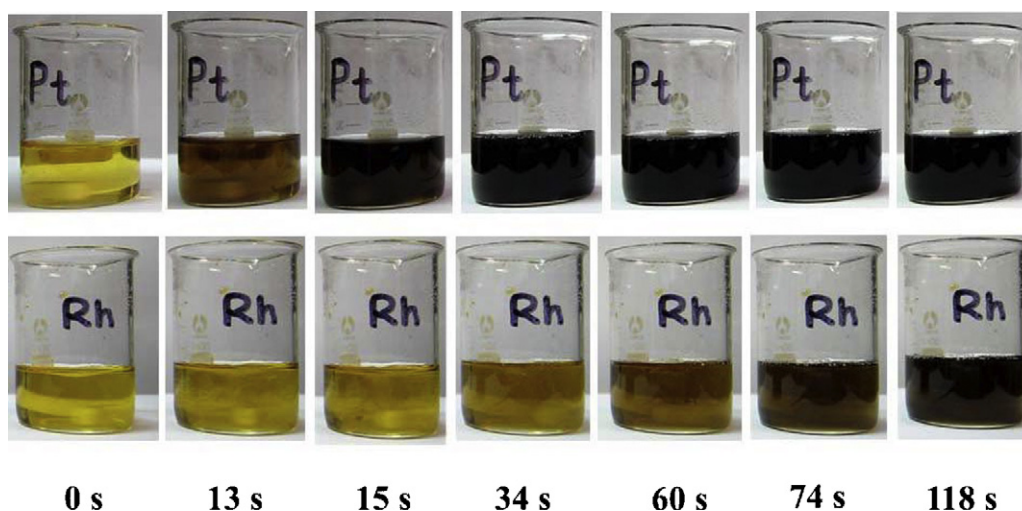


Fig. 2. The photos at different time during the reduction procedure of PtCl_4^{2-} and Rh^{3+} in ethylene glycol by adopting NaBH_4 as the reducing agent.

As it can be clearly seen in Fig. 4A, the XRD patterns of PtSnRh/C show a broad face-centered cubic (fcc) structure indicating a very small average particle size of the catalyst. After heat treatment, the corresponding diffraction peaks of Pt become sharp and obvious, demonstrating that the heat treatment makes the particle size bigger. This can also be clearly observed from TEM results (Fig. 5). In Fig. 4A one can distinguish that in the case of PtSnRh/C, the corresponding diffraction peaks of Sn or SnO_x and Rh do not exist. This could be due to the too small particle size and the difficulty to identify them. Moreover, Rh has very similar lattice parameters to Pt, and this makes it difficult to distinguish their peaks [8]. While, in the case of PtSn@Rh/C, it can be distinguished from Fig. 4B that except for the obvious diffraction peaks of Pt, the main diffraction peaks of SnO_2 can also be detected. The diffraction peaks of Rh are still difficult to find due to the similarity of lattice parameters of Pt and Rh. However, a weak Rh (3 1 1) diffraction peak can still be observed (Fig. 4B).

TEM results show that after deposition on the carbon support and thermal treatment, both PtSnRh and PtSn@Rh take on in the form of nanospheres, which are evenly distributed on the carbon support. It can also be seen that the thermal treatment brings out a

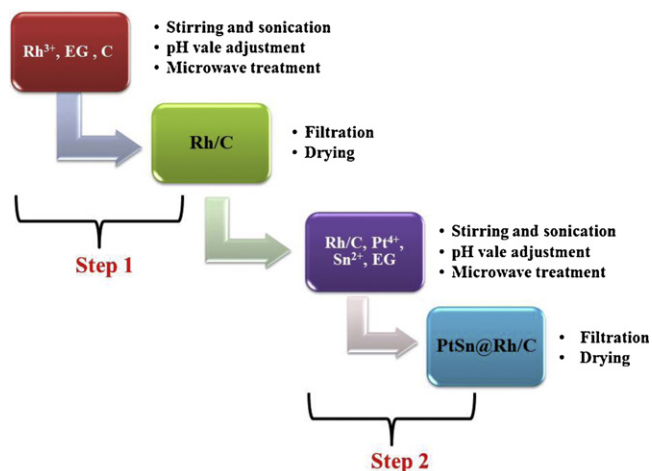


Fig. 3. The schematic presentation for two-step preparation of PtSn@Rh/C catalysts without and with heat treatment.

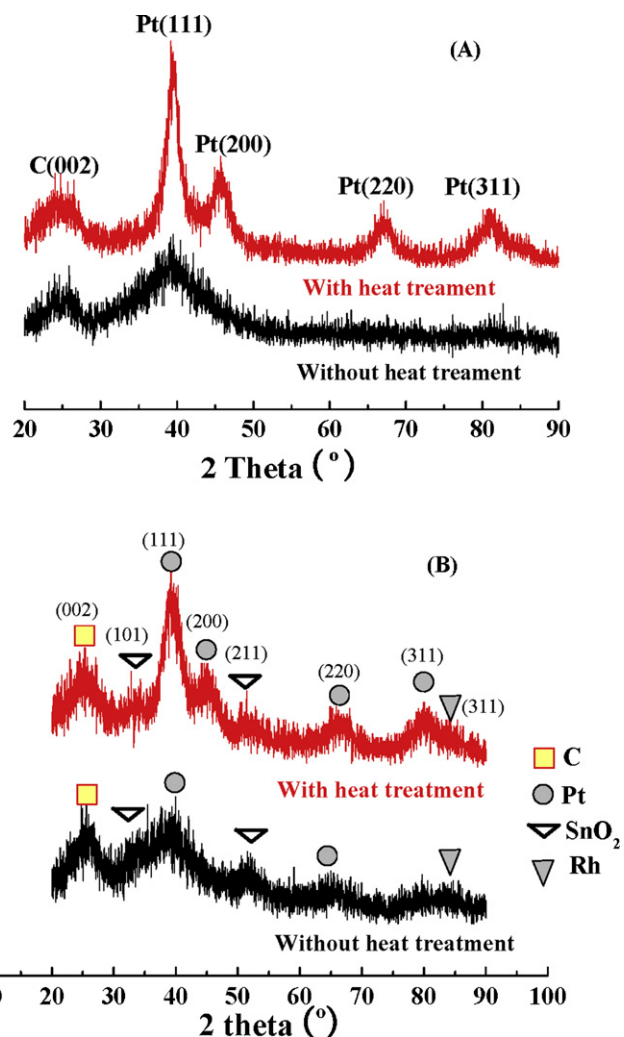


Fig. 4. XRD spectra of the as-prepared PtSnRh/C (A) and PtSn@Rh/C (B) without and with heat treatment.

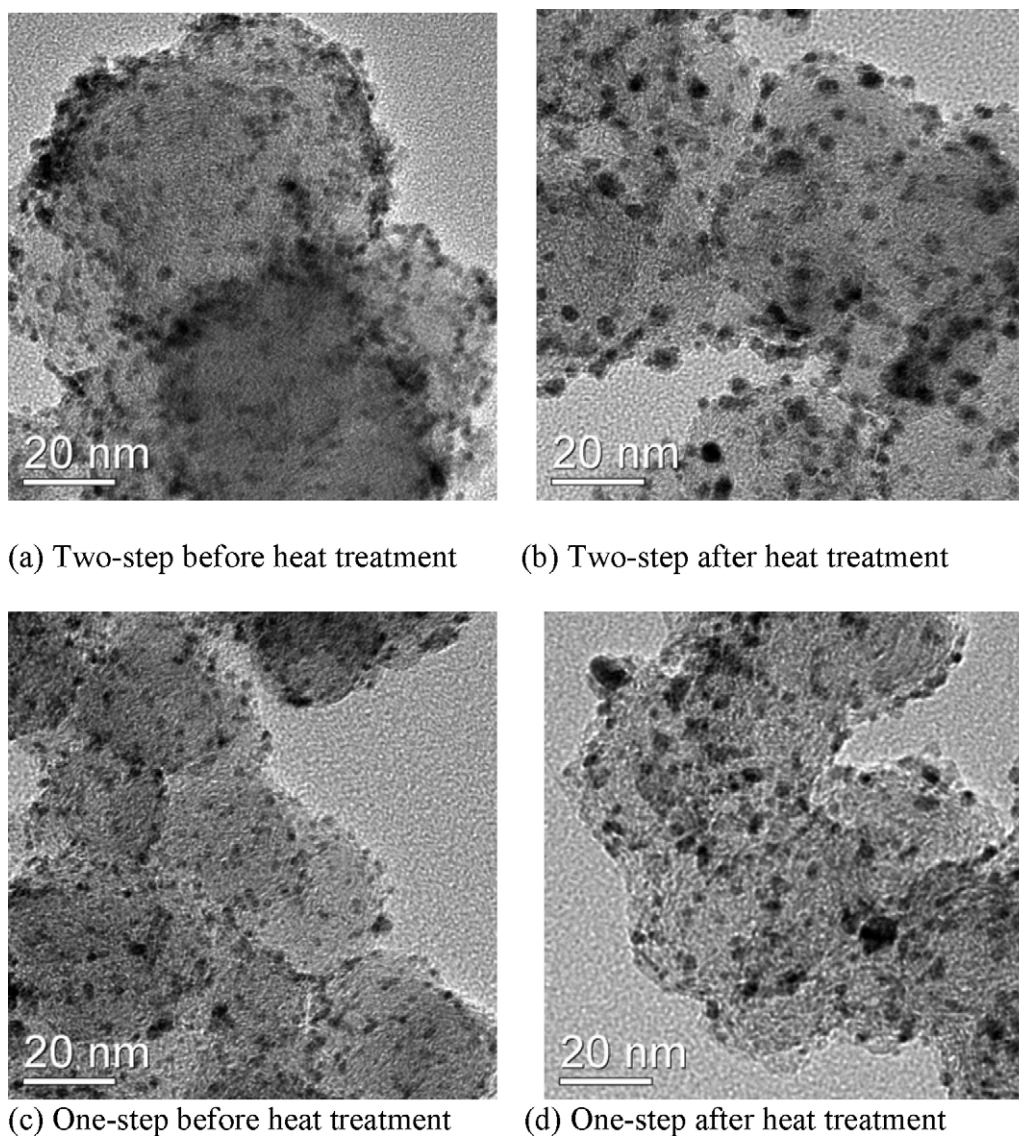


Fig. 5. TEM images of the PtSn@Rh/C (A and B) and PtSnRh/C (C and D) without and with heat treatment.

bigger particle size of the catalysts. This agrees well with the above XRD results.

The corresponding CVs results of PtSn@Rh/C without and with heat treatment are given in Fig. 6. It is found that with PtSn@Rh/C-HT as the catalyst, not only the activity of ethanol electrooxidation but also the activity of its immediate products (acetaldehyde, and acetic acid) electrooxidation is obviously higher than those at PtSn@Rh/C-AP. As generally found, in the case of ethanol and acetaldehyde electrooxidation, the enhanced activity can be reflected in the form of negatively shifted onset potential and increased current density. More interestingly, in the case of acetic acid electrooxidation, there is a noticeable oxidation current at PtSn@Rh/C-HT, suggesting the high electrocatalytic activity of the as-synthesized PtSn@Rh/C-HT toward acetic acid electrooxidation. This could be due to the following reasons. With heat treatment, the mutual effect between these three components has been enhanced. Simultaneously, the heat treatment with reductive gas can lead to part reduction of SnO_2 into Sn and then more Sn interaction with Pt and Rh. Consequently, though the PtSn@Rh catalyst is less reactive for ethanol dissociative adsorption due to the lower d band

center, it could be more active toward ethanol oxidation [10]. This is because Pt/Sn/Rh has a weaker bind to blocking intermediates, making it more resistant to poisoning [10]. Moreover, the corresponding characteristic peaks for hydrogen adsorption/desorption disappear. This is not the same in the case of Pt or PtSn catalysts [16,17], where there is almost no featureless CV profile for acetic acid electrooxidation, while exist even stronger peaks for hydrogen adsorption/desorption. This could be attributed to the adsorption and decomposition of acetic acid on Rh [18]. The further oxidation of acetic acid means the C–C bond cleavage, suggesting that a higher CO_2 selectivity and thus higher faradaic efficiency could be obtained for ethanol electrooxidation over PtSn@Rh/C-HT.

In order to further check the activity of PtSn@Rh/C-HT, the PtSnRh/C-HT obtained by one-step method followed by heat treatment was adopted as the counterpart. It can be clearly seen from Fig. 7 that PtSn@Rh/C-HT exhibits superior activity towards all ethanol, acetaldehyde, and acetic acid oxidation to PtSnRh/C-HT. One possible reason is that in the process of two-step sequence synthesis of PtSn@Rh/C, Rh was solely and firstly deposited onto

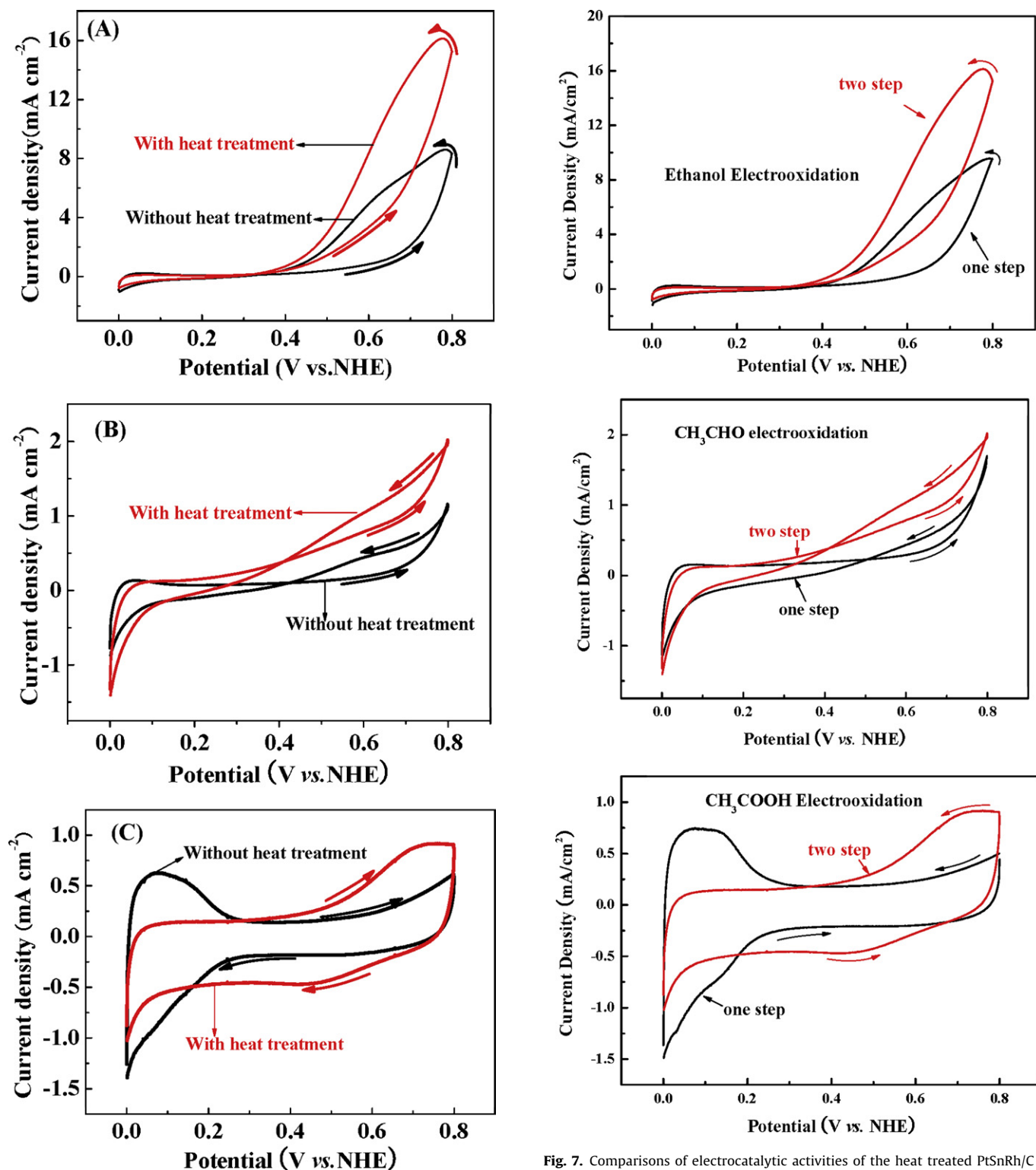


Fig. 6. Comparisons of electrocatalytic activities of PtSn@Rh/C without and with heat treatment towards C_2H_5OH , CH_3CHO , and CH_3COOH , temperature $30^\circ C$, scan rate: 50 mVs^{-1} . CV curves in 0.5 mol L^{-1} H_2SO_4 aqueous solutions containing 1.0 mol L^{-1} C_2H_5OH (A), 0.5 mol L^{-1} CH_3CHO (B), and 0.5 mol L^{-1} CH_3COOH (C).

carbon support and thus Rh could be thoroughly reduced. Following this, the Pt and Sn precursors were introduced, avoiding the part blockage of Pt active sites. Here, it should be noted that although heat treatment had a significantly improved effect on PtSn@Rh/C

Fig. 7. Comparisons of electrocatalytic activities of the heat treated PtSnRh/C by one-step and PtSn@Rh/C by two-step towards C_2H_5OH , CH_3CHO and CH_3COOH , temperature $30^\circ C$, scan rate: 50 mVs^{-1} . CV in 0.5 mol L^{-1} H_2SO_4 aqueous solutions containing 1.0 mol L^{-1} C_2H_5OH (A), 0.5 mol L^{-1} CH_3CHO (B), and 0.5 mol L^{-1} CH_3COOH (C).

electrochemical activity, it almost takes no effect in the case of PtSnRh/C by the one-step method as can be seen from Fig. 8.

PtSn@Rh/C-HT was also compared with the PtSn/C recognized as best ethanol electrooxidation catalysts and Pt/C and the results are given in Fig. 9. In the case of ethanol electrooxidation (Fig. 9A), the activity of catalysts follows the order of PtSn/C > PtSn@Rh/

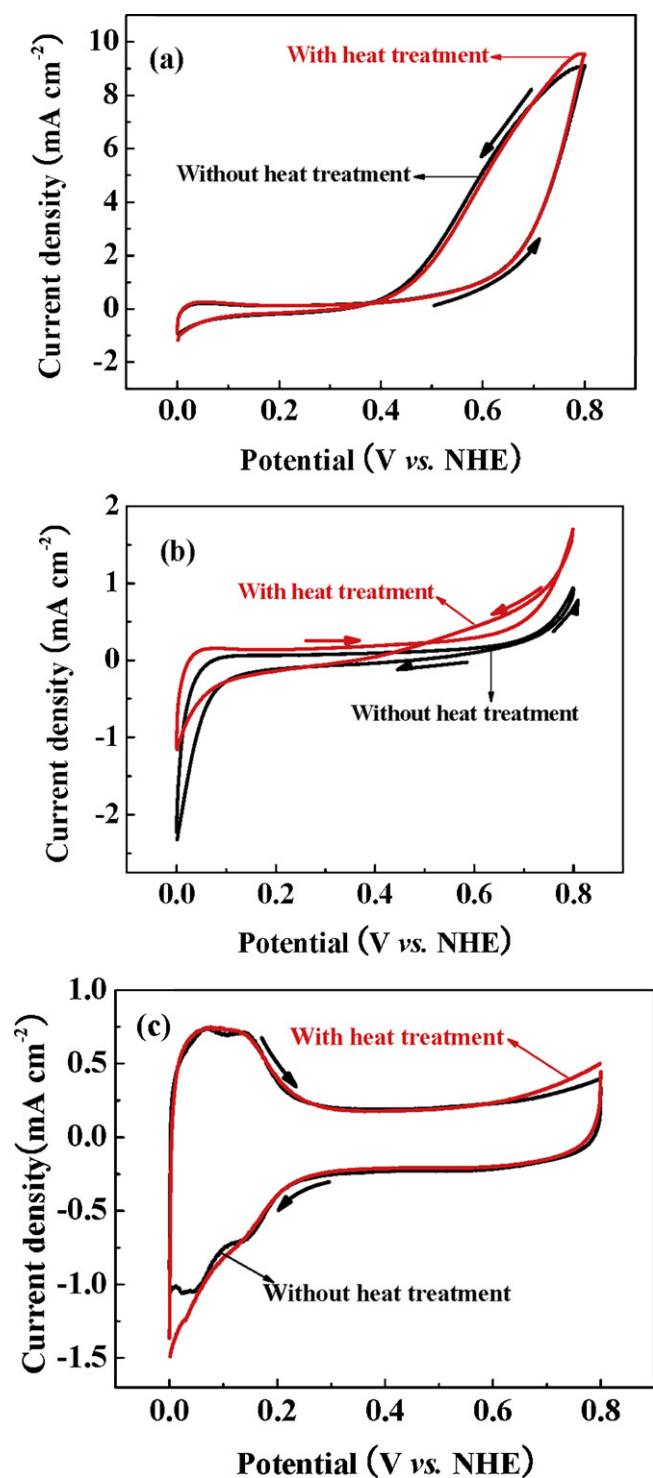


Fig. 8. Comparisons of electrocatalytic activities of PtSnRh/C without and with heat treatment towards $\text{C}_2\text{H}_5\text{OH}$, CH_3CHO and CH_3COOH , temperature 30°C , scan rate: 50 mV s^{-1} . CV curves in $0.5\text{ mol L}^{-1}\text{ H}_2\text{SO}_4$ aqueous solutions containing $1.0\text{ mol L}^{-1}\text{ C}_2\text{H}_5\text{OH}$ (A), $0.5\text{ mol L}^{-1}\text{ CH}_3\text{CHO}$ (B), and $0.5\text{ mol L}^{-1}\text{ CH}_3\text{COOH}$ (C).

C-HT > Pt/C. It can be anticipated that Pt/C gives the lowest activity due to the high potential of water dissociation at Pt and its easy being attacked by poisoning species. PtSn/C performs best due to the cooperative effect between Pt and Sn. In the case of PtSn@Rh/C-HT, in spite of the absence of Pt blockage by Rh, the Pt content is lower than that in PtSn/C.

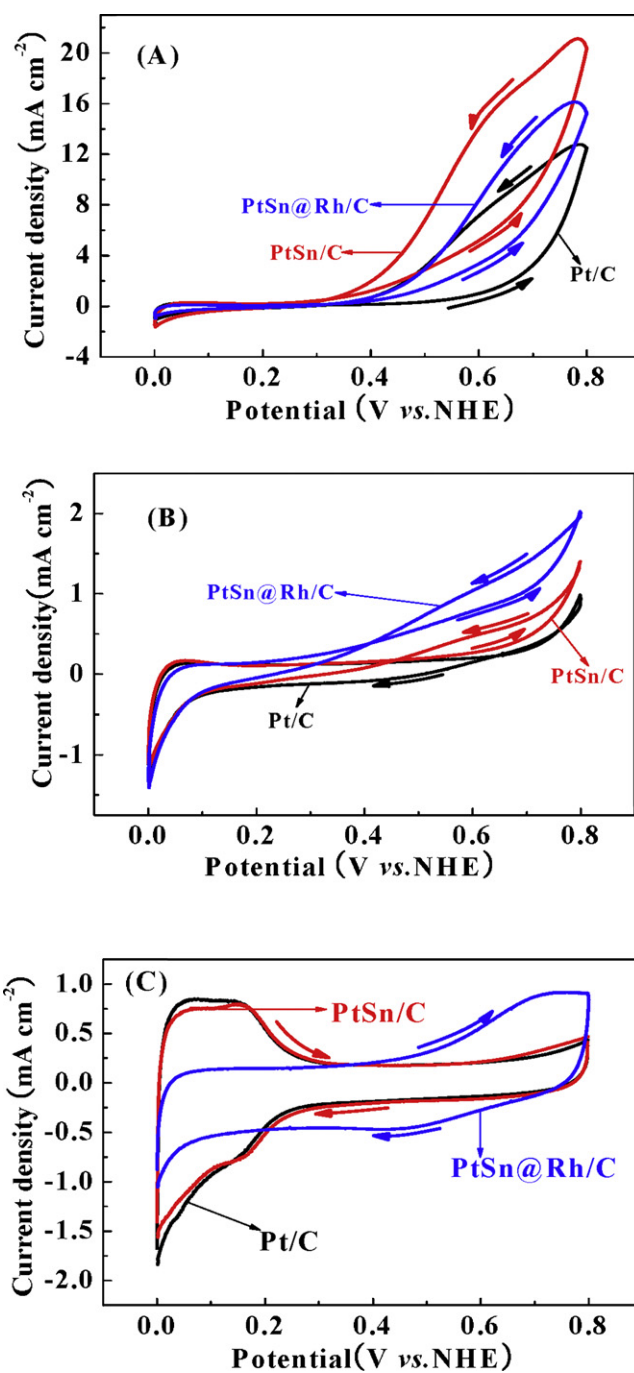


Fig. 9. Comparisons of electrocatalytic activities of Pt/C, PtSn/C and heat treated PtSn@Rh/C towards $\text{C}_2\text{H}_5\text{OH}$, CH_3CHO and CH_3COOH , temperature 30°C , scan rate: 50 mV s^{-1} . CV curves in $0.5\text{ mol L}^{-1}\text{ H}_2\text{SO}_4$ aqueous solutions containing $1.0\text{ mol L}^{-1}\text{ C}_2\text{H}_5\text{OH}$ (A), $0.5\text{ mol L}^{-1}\text{ CH}_3\text{CHO}$ (B), and $0.5\text{ mol L}^{-1}\text{ CH}_3\text{COOH}$ (C).

4. Conclusion

Here we demonstrated the preparation of PtSn@Rh/C catalysts by a two-step sequence by the modified pulse microwave assisted polyol method, followed by the heat treatment in a reductive atmosphere. The heat-treated PtSn@Rh/C exhibited significantly enhanced activity towards the electrooxidation of ethanol as well as its oxidation intermediate products (acetaldehyde and acetic acid) compared to the untreated PtSn@Rh/C and PtSnRh/C by the one-step method. Especially, the heat-treated PtSn@Rh/C showed quite different behavior

for acetic acid electrooxidation, with the disappearance of characteristic peaks for hydrogen adsorption–desorption and obvious oxidation current peaks. This suggests that the C–C bond cleavage happened over the heat-treated PtSn/Rh/C. The present research work presents a promising catalyst preparation method for optimizing Pt–Sn–Rh ternary catalysts for oxidizing ethanol with high activity and high selectivity towards CO₂.

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